High-dimensional quantum dynamics of adsorption and desorption of H₂ at Cu(111)

Axel Gross, Bjørk Hammer*, and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Wilhelm Brenig

Physik-Department T30, Technische Universität München, D-85747 Garching, Germany

We performed high-dimensional quantum dynamical calculations of the dissociative adsorption and associative desorption of H₂/Cu(111). The potential energy surface (PES) is obtained from density functional theory calculations. Two regimes of dynamics are found, at low energies sticking is determined by the minimum energy barrier, at high energies by the distribution of barrier heights. Experimental results are well-reproduced qualitatively, but some quantitative discrepancies are identified as well.

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Dissociative adsorption is one of the crucial steps in heterogenous catalysis. This has motivated, apart from its fundamental interest for surface chemistry, a large number of studies on well defined model systems where the dissociative adsorption process can be investigated in detail. The system which has been studied to the largest extent is H₂/Cu(111) (see, e.g., [1,2]). For this system the adsorption is hindered by a noticable energy barrier. It has been found that the dissociative adsorption of hydrogen approximately obeys normal-energy scaling [3], which means that the sticking probability is only determined by the component of the molecule's momentum perpendicular to the surface. Usually normal-energy scaling is associated with a flat, structureless surface. For the (111) metal surface this seemed to be an appropriate description as this is the most densely packed surface.

Indeed the *electron density* at clean metal (111) surfaces shows only a small corrugation of less than 0.1 Å at a distance of 1 Å above the center of the surface layer [4]. However, adsorption properties are determined by the local chemical interaction on the surface. In recent total energy calculations [5] using density functional theory (DFT) together with the generalized gradient approximation (GGA) [6] for the exchange-correlation functional, the potential energy surface (PES) for H₂/Cu(111) has been determined. Besides the GGA the main approximation is due to the super-cell approach and the **k**-summation. A rather strong corrugation is found when all six degrees of freedom of the H₂ molecule are varied. For a 4-layer substrate with the molecular axis kept parallel to the surface, which is the most favorable configuration for dissociation, the energy barrier to adsorption varies between 0.73 eV and 1.43 eV within the surface unit cell. Also the distance of the barrier from the surface and the extension of the hydrogen bond at the barrier region strongly depend on the point of impact in the unit cell and the orientation of the molecule.

In order to investigate the consequences of the strong corrugation on the adsorption and desorption dynamics, we have taken the GGA-PES as an input for a quantum dynamical simulation. We use a five-dimensional parametrization of the results obtained for the 4-layer substrate with the molecular axis being kept parallel to the surface as for this configuration the lateral corrugation of the PES has been determined in great detail in the DFT calculations. Although the polar rotation of the molecule is not considered, to our knowledge this is the first study of the influence of lateral corrugation on the quantum dynamics of adsorption and desorption which takes into account such a large number of degrees of freedom using a realistic PES. Because of the high-dimensionality of the calculations, the comparison of the results with experimental data for the H₂/Cu(111) system will in addition provide information about the accuracy of the theoretical GGA-PES. We will show that the GGA-PES reproduces the experimental findings qualitatively well, but some quantitative differences are identified. We will demonstrate the importance of the corrugation of the PES for the adsorption dynamics, the angular dependence of the sticking probability, the mean kinetic energy in desorption, and the desorption flux.

The quantum dynamics is determined by solving the time-independent Schrödinger equation for the H₂ molecule moving in the GGA-PES. We use the concept of the *local reflection matrix* (LORE) [7] and the *inverse local transmission matrix* (INTRA) [8]. The propagation of the reflection and inverse transmission matrices on an accurate piecewise constant representation of the PES avoids exponentially increasing evanescent waves whereby numerical instabilities are prevented. The center of mass distance of the molecule from the surface Z, its two surface coordinates X and Y and the interatomic molecular spacing r are taken as dynamical variables. The molecular azimuthal orientation is treated as a fixed parameter in the adsorption simulation, and all theoretical results are then obtained by averaging over twelve different orientations. This is a reasonable approximation because the molecular rotation is a slow process. For instance, an H₂ molecules with a kinetic energy of 0.5 eV in the rotational state $J = 4$ corresponding to an rotational energy of 0.15 eV rotates only once in the

time it takes to move forward 4.2 Å, while the interaction range of the potential is 0.5 Å.

The local nature of LORE and INTRA does not only give information about final transition probabilities, but also about the scattering solution of the wave function everywhere in space [9]. To give an idea about the size of the corrugation of our PES and its consequences on the dynamics we have plotted in Fig. 1 the positive real part of the wave function for an incident beam with total kinetic energy $E_i = 1.08$ eV and incident angle $\theta_i = 45°$ scattered at a surface with one-dimensional lateral corrugation having the same variation in energy and location of the barrier as the full potential. The sticking probability is given by the flux of the particles that traverse the barrier. To make both the incoming plus transmitted and the reflected part of the beam visible in one *single* plot, we have restricted in the plot the lateral extension of the beam perpendicular to its propagation direction, which is in principle infinite. The splitting of the beam in a reflected and a transmitted part can be traced very clearly. Also the development of the different diffraction beams can be followed.

In Fig. 2 we show results for the sticking probability as a function of the normal kinetic energy of the incident H_2 beam initially in the vibrational ground state for various polar angles of incidence ($\theta_i = 0°$ refers to normal incidence). Furthermore we present results for two-dimensional calculations corresponding to non-corrugated surfaces with the minimum and maximum barrier of the fully corrugated surface. Also a sticking curve derived from experiment [10] is shown. For $\theta_i = 0°$ two energy regimes can be separated. At low energies (Fig. 2b) the "5D" sticking curve for the corrugated surface is parallel to the 2D sticking curve for the non-corrugated surface with the minimum energy barrier. The 2D sticking curve for the maximum barrier is suppressed by more than ten orders of magnitude and has a different slope. These results indicate that the "5D" data can be explained by a kind of key-hole effect. Since sticking at these energies can only be achieved by tunneling, it is very sensitive to the barrier height. The sticking for normal incidence at low energies is therefore determined by the molecules which hit the surface within the lowest energy configuration; molecules which hit the surface at unfavorable sites or with unfavorable orientation do practically not contribute to the sticking.

For incident energies larger than approximately 0.6 eV the slope of the sticking curve for the corrugated surface in the logarithmic plot changes. At this energy adsorption without tunneling becomes possible since the effective minimum barrier height is reduced by 0.15 eV for molecules in their vibrational ground state due to the softening of the H_2 bond at the surface and the accompanied reduction of the zero-point vibrational energy. In the linear plot (Fig. 2a) the sticking curve obtained for the corrugated surface connects the onset of sticking for the minimum barrier approximately linearly with the point where the sticking probability in the maximum barrier system reaches unity. Test calculations with a changed barrier widths but unchanged barrier heights yield almost unchanged sticking probabilities at these energies. These facts indicate that the sticking probability in this energy range is determined by the distribution of the barrier heights. This is the first multidimensional evidence that for large energies the sticking can be understood in terms of the region of the surface that classically is available to dissociation, which is an important assumption in the so-called hole-model [11].

The comparison of the experimentally derived sticking curve with the theoretical results for the high-dimensional PES shows that the increase for sticking probabilities between 0.01 and 0.4 is actually similiar. The main difference in this range of sticking probabilities is that the theoretical results appear at energies which are too high by about 0.2 eV. This indicates that the minimum energy barrier for dissociation of the GGA-PES should be lowered from 0.73 eV to about 0.5 eV. In fact, convergence tests reported in Ref. [5] have shown that such a lowering of the barrier is to be expected.

For low and for high energies, however, the theoretical sticking probabilities are at variance with the experiment. The experimental curve has been derived by fitting existing adsorption data and desorption data via the principle of detailed balance to an assumed functional form of the sticking curve [10]. In detailed balance the desorption flux is determined by the product of the sticking probability, which increases exponentially in the low-energy regime, with the exponentially decreasing Boltzmann factor, resulting in a desorption flux which is strongly peaked at energies close to the minimum barrier height. Beam adsorption data, which are only available up to energies of about 0.5 eV for H_2 [10], are dominated at low energies by the initially vibrationally excited molecules [3]. Thus at least for initially non-vibrating molecules the fitting procedure might not be very sensitive at low and high energies. For energies close to the minimum barrier height the agreement between our results and experiment (except for the energy shift) suggests that the spatial corrugation of our PES resembles that of reality. This also implies that the width of the experimentally derived sticking curve does not correspond to the barrier width [12], but to the distribution of barrier heights since it is this distribution which determines the increase of the sticking probability in this range.

Just recently it has been pointed out [13] that, apart from the change in momentum of inertia, an isomorphism exists between surface corrugation and a planar rotor. This can be used to give an estimate about the effect of dynamically including the rotations. The total energy for a rotated H_2 dimer has been calculated: At the optimum reaction configuration the energy required to turn the molecule upright is 0.4 eV [5] which is of the or-

der of the lateral corrugation. Thus taking into account the rotation will have a similar effect as including the surface corrugation, namely that for $J = 0$ in the low energy regime the sticking probability will basically be suppressed by a constant factor due to the smaller keyhole in phase space, while in the high energy regime the energy at which the sticking probability reaches one will be shifted to larger energies due to the existence of higher barriers. The onset of the high energy regime will not be changed since the minimum barrier will remain the same.

For non-normal incidence also two energy regimes can be separated. At high energies (above 0.6 eV, see Fig. 2a) the sticking obeys normal-energy scaling in agreement with the experiment although the surface is strongly corrugated. This issue has already been addressed by Darling and Holloway [14]. Using model potentials they showed that the variation of the barrier height and the variation of the barrier position have opposing effects as far as the role of addional parallel momentum for adsorption is concerned. If the maximum barriers are at a greater distance from the surface these opposing effects cancel to a large extent leading to approximate normal-energy scaling even for strongly corrugated surfaces [14]. The GGA-PES shows these features (see Fig. 1) indicating that this explanation also applies to our calculations including the full lateral corrugation.

However, Fig. 2b reveals that in the low energy range, which had not been considered in Ref. [14], additional parallel momentum helps to cross the barrier. The situation is shown in Fig. 1. A large part of the transmitted fraction of the beam propagates through the minimum barrier site without moving like a classical particle, but being steered in the tunneling process to the energetically most favorable propagation path thereby converting parallel into normal energy, which in turn increases the tunneling probability [15].

In Fig. 3 the mean kinetic energy of desorbing molecules versus desorption angle at a surface temperature of $T_s = 925$ K is plotted. Measurements by Comsa and David [16] have shown that the kinetic energy is independent of the desorption angle, which is surprising taking into account normal energy scaling for H_2/Cu(111) in a classical model (solid line in Fig. 3). This issue has been discussed at length by Michelsen and Auerbach [10] who showed via detailed-balance arguments that due to the significant width of the sticking probability, which effectively changes with desorption angle, a constant mean kinetic energy in desorption can be achieved even under the assumption of normal-energy scaling. Our calculations also give a kinetic energy of desorbing molecules almost independent of the desorption angle. Here it is mainly due to the inclusion of geometric corrugation which makes parallel momentum more effective for traversing the barrier leading to a more isotropic distribution of desorbing molecules [15].

The mean kinetic energy obtained in our "5D" quantum dynamical calculation is 0.2 eV larger than the one measured in experiments [16,17]. This again corresponds to the shift in the minimum energy barrier height of our PES as discussed above. The vibrational excitation of desorbing molecules at $T_s = 925$ K is calculated to be 0.87% while the experimental result is 2.9% [17]. The GGA places the energy barrier for dissociation correctly in the "exit" channel in the rZ-plane (see Fig. 1a in [5]). However, the H_2 bond length at the barrier top is only extended by 33% so that the barrier position is still too early [18,19].

Calculations using only a two-dimensional PES with the minimum energy path yield 0.67 eV for the mean kinetic energy and 0.83 % for the vibrational excitation in desorption at $T_s = 925$ K. These numbers are relatively close to the ones derived for a fully corrugated surface indicating that most desorbing molecules follow the minimum energy path. This shows that it is justified to *neglect corrugation* in the simulation of *desorption processes* if there is one preferred reaction path to desorption which is energetically much more favorable than all others.

The calculated angular distribution of desorbing molecules can be fitted to a $\cos^n \theta$-curve with $n \approx 25$. This distribution is narrower than the one seen in experiments which yield an exponent of $n_{exp} \approx 8$ [16]. This can partly be attributed to the fact that the kinetic energy of desorbing molecules is too high in our calculations. Furthermore, experiments have shown that the angular distribution in desorption is broadened if the motion of the surface atoms is taken into account [20], which is neglected in our calculations.

In conclusion, we have presented a dynamical study of the dissociative adsorption and associative desorption in the system H_2/Cu(111) using a five-dimensional potential energy surface which has been determined by *ab initio* calculations in the generalized gradient approximation. Except for an energy shift of 0.2 eV due to the restricted super cell and **k**-point set, the GGA-PES describes the surface corrugation qualitatively well. In the tunneling regime sticking is determined by the minimum energy barrier. For energies larger than the effective minimum barrier height the width of the sticking curve corresponds to the distribution of barrier heights, and sticking obeys normal-energy scaling although the PES is strongly corrugated. The mean kinetic energy of desorbing molecules is almost independent of the desorption angle due to the variation of the barrier location. In order to simulate desorption experiments corrugation can be neglected if there is one energetically favorable reaction path to desorption.

* Present address: Physics Department, Technical University of Denmark, DK-2800 Lyngby, Denmark.

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FIG. 3. Mean kinetic energy of desorbing molecules versus desorption angle at a surface temperature of $T_s = 925$ K obtained in our quantum dynamical calculation (open circles) and in a classical model for a flat surface (after Ref. [16]) with the minimum energy barrier of 0.73 eV.

FIG. 1. Positive real part of the wave function of H_2 scattered at a PES with one-dimensional lateral corrugation simulating H_2/Cu(111). The incident beam has a kinetic energy of $E_i = 1.08$ eV, the incident angle is $\theta_i = 45°$. The contour spacing for the potential (thick lines) is 0.1 eV. The positions of the Cu atoms are at the potential maxima.

FIG. 2. Sticking probability versus normal kinetic energy for molecules initially in the vibrational ground state. a) Linear plot, b) logarithmic plot (note the different energy range). 5D-calculations for different incident angles at the corrugated surface: solid line $\theta_i = 0°$, $\diamond$ $\theta_i = 15°$, $\triangle$ $\theta_i = 30°$, $\bigcirc$ $\theta_i = 45°$; 2D-calculations corresponding to a flat surface: dash-dotted line for the minimum barrier, long-dashed line for the maximum barrier. Dashed line: Experimental curve incorporating adsorption data and, via the principle of detailed balance, also desorption data (from Ref. [10]).

Figure b) Sticking probability versus Normal kinetic energy (eV), with curves for 5D, $\theta_i = 0°$; 5D, $\theta_i = 15°$; 5D, $\theta_i = 30°$; 5D, $\theta_i = 45°$; 2D, min. barrier; 2D, max. barrier; and experiment.